REVIEW OF COLLOIDS IN ORE GENESIS

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ABSTRACT.

Advances in the theory of colloidal chemistry over the past decade indicate that this state of matter may take part in ore forming processes to a far greater extent than is at present generally recognised.

The stability of a colloidal sol system is subject to; temperature, pressure, pH, ions in solution, and other colloidal species present. Most sulphide sols are stabilized in the presence of hydrogen sulphide, even to such an extent that NaCl and KCl may not cause coagulation. Silica sol probably has a very important stabilizing effect on most metal hydrosols. In many sol systems the pH of the solution determines the charge on individual particles and thus the degree of dispersion. The effect of temperature on sol stability is unknown but recent work tends to suggest that in some cases increased temperature results in decreased stability.

Colloform (globular, framboidal, oolitic, reniform and botryoidal) textures have been successfully produced in the laboratory from sulphide gels. Such textures may also develop due to crystallization from true solutions, but structural criteria exist to differentiate the two origins. Ore textures exhibiting a crystalline form do not necessarily indicate precipitation from true solutions as crystalline textures may equally develop due to ageing of gels.

There is no inter-dependence between the transport of metals as colloidal sols and their deposition as colloidal gels. Fluid inclusions present in minerals precipitated via the gel stage, may give little information on the composition of the ore fluid, or the temperature of precipitation.

1. INTRODUCTION.

Many investigators in the field of ore genesis consider the participation of colloids in ore transport and deposition as very minor or non-existent. This review underlines the physical and chemical properties of colloidal systems and attempts to indicate how these properties might determine the role of colloids under the geological environments prevailing during ore transport and deposition.

The existence of colloidal systems compared with true solutions, in ore fluids, must not be ruled out on the basis of the predominance of the latter in our natural surroundings. On the contrary, colloidal systems are common in natural environments, e.g., dispersed clays, swamp water, milk, eggs and proteins.

There are three important ways in which colloids may play a significant part in ore genesis.

(a) Transportation of the metals as stable sulphide or hydroxide sols.

(b) Adsorption of metal ions onto colloidal clay or silica particles during sedimentation, with subsequent desorption during diagenesis.

(c) Deposition of the ores as simple or complex gels.

These three processes will be developed throughout the review.

The writer acknowledges with gratitude the assistance of Mr. J.N. Elliston of Peko-Wallsend Ltd., who provided a valuable list of references, and whose early discussions instigated the study.

2. DEFINITIONS OF COLLOID SYSTEMS.

The term "colloids" was introduced by Graham in 1861, and derives from the Greek word for glue. He was referring to substances which showed a very slow diffusion velocity "in solution" compared with sugar and salts. The characteristics associated with colloids have subsequently been found to result from their exceedingly high surface area per unit volume. A substance is thus defined as colloidal, or in a colloidal state, if it consists of very fine particles dispersed within a homogeneous medium. The size limits of the dispersed particles are not definitely fixed, but are generally stated as $10^{-3}\mu$ to 1μ. At particle sizes less than $10^{-3}\mu$ the colloidal sol merges into true solution while above 1μ it merges into a suspension.

Almost any substance can be obtained in the colloidal state provided a method is available for acquiring particles within the desired size range. Eight distinct types of colloid systems are recognised, being defined according to the phase of the dispersed particles and the dispersion medium. Of these, the sol, gel and foam systems are the ones of most importance in geological environments.

A sol is the colloid system in which solid particles are dispersed in a liquid medium.

A gel is the system in which the colloidal particles constitute a coherent structure which is inter-penetrated by a liquid.

A foam is the system in which gas particles are dispersed in a liquid medium.

3. CLASSIFICATION OF COLLOID SYSTEMS.

The most important classes of hydrous sol systems (hydrosols) are classified according to the affinity of the dispersed particles for water. Colloids which contain little absorbed water, and consist of small solid particles or molecular aggregates whose behaviour is dominated by surface effects, are known as hydrophobic colloids. Examples include metal sols, sulphide sols, silver halides and many insoluble salts. Colloids in which the particles display a marked affinity for water are known as hydrophillic colloids. This type include silicic acid, tungstic acid and gelatin. In general the hydrophobic colloids are less stable and more easily coagulated than the hydrophillic variety. The differences between the two types are not distinct and some substances such as the hydroxides of iron and aluminium show affiliation with both groups.

Colloids may also be classified according to the structure of the dispersed particles. Three types are distinguished,

(a) Micellar colloids in which the dispersed particles consist of aggregates formed from smaller molecules, e.g., sulphide sols, insoluble salt sols.

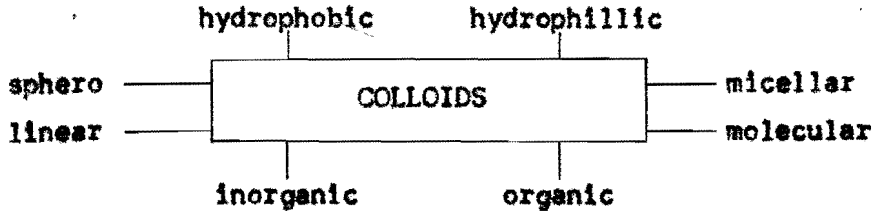
(b) Molecular colloids with molecules so large in size that they exist in the colloidal size range, e.g., silicones, proteins.

(c) Small particles having the same structure as the bulk solid, e.g., gold sol.

A classification of colloids according to the shape of the dispersed particles (sphero or linear) has proved very useful, as many important physical properties depend on particle shape. For example, the spherocolloids show little swelling, produce low viscosity solutions and do not readily form gels,

whereas the linear colloids show considerable swelling, produce high viscosity solutions, and possess a strong ability to form gels.

The various classifications of colloids are summarized below in the diagram after Jirgensons and Straumanis (1962).



4. SOL SYSTEMS.

4.1 Charge on sol particles.

Under the influence of an electric field sol particles move preferentially towards one electrode; a process known as electrophoresis. The obvious conclusion is that particles are charged and migrate towards the electrode of opposite sign. This surface charge may develop due to one of two phenomena.

(a) Considering the colloidal particles as fragments from a continuous crystal lattice, then a net positive or negative charge will develop on the surface of the particle if imperfections occur within the interior of the lattice fragment. This is the origin of the surface charge of clay systems, but is unusual for other hydrophobic sols. (Olphen, 1966).

(b) Alternatively the sol particles may become charged due to preferential adsorption of specific ions onto the particle surface. Such adsorption occurs due to three processes. (i) Chemical bonding of the ions to the surface (chemisorption) or electrostatic bonding via Van der Waals forces or hydrogen bonds. (ii) Adsorption of a similar ion to that forming the lattice of the particle. (iii) Adsorption of hydroxyl ions resulting in hydrolysis of the surface of the sol particles.

Hydrophobic sols commonly obtain their charge by adsorption of ions identical with those forming the particle lattice (process ii). Olphen (1966) gives the silver iodide sol as a typical example. In this case, due to the slight solubility of silver iodide, both Ag^+ and I^- ions are present in solution, the solubility product K_{sp} being given by;

$$K_{sp} = \left[Ag^+\right]\left[I^-\right]$$

If the equilibrium between Ag^+ and I^- ions in solution is upset by the addition of a soluble compound of one of these ions (e.g., $AgNO_3$), then the ion of maximum concentration (Ag^+) will pass out of solution and adsorb on the lattice surface, occupying a regular lattice position. The surface then has vacant I^- sites and is positively charged. Equivalently if I^- ions were added to the system, the sol particles would attain a negative surface charge. It is thus evident that the ratio of Ag^+/I^- ions in solution determines the sign of the sol particles. At some intermediate ratio of Ag^+/I^-, the particles will have no charge. This condition is known as the zero point of charge (Z.P.C.)

The metallic hydroxide sols, which show a partial hydrophillic character, are also charged by the above mechanism. In this case the ratio of metal ion (M^{n+}) to hydroxyl ion (OH^-) will depend on the pH of the system. Thus in strongly alkaline solutions the particle surface is negatively charged, while in acid solutions the surface is positively charged. This situation is represented in fig. 1.

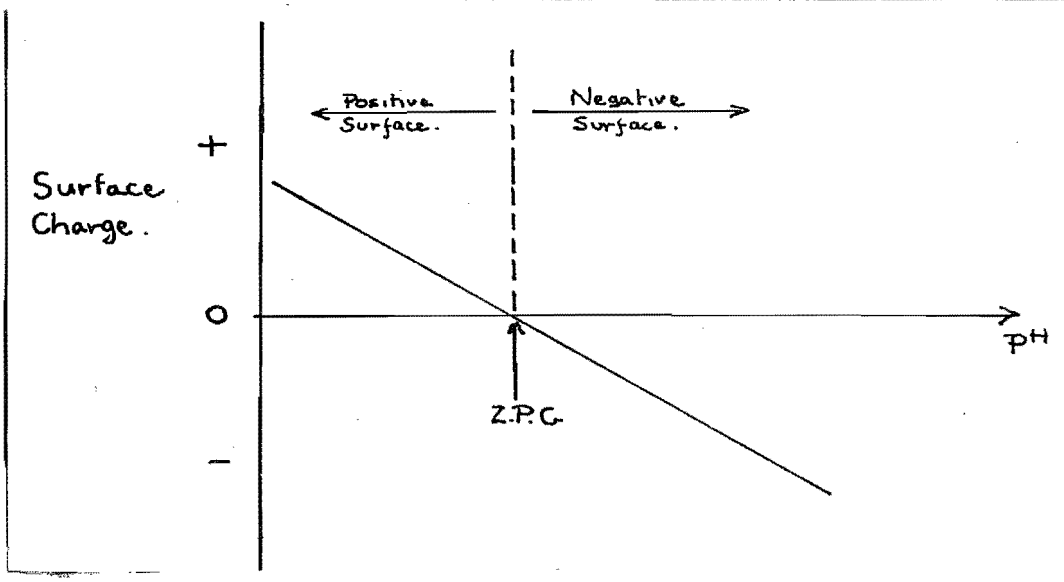


Fig.1. Schematic representation of the variation of surface charge with pH for the metal hydroxides.

Consider an $M(OH)_n$ sol in a strongly alkaline solution. OH^- ions will be adsorbed onto the particles in lattice site positions, thus generating a negative surface charge. If the pH of the system is decreased by the addition of hydrogen ions, then OH^- ions will be subtracted from solution by the association; $H^+ + OH^- \rightleftharpoons H_2O$. The equilibrium between M^{n+} and OH^- ion in solution is upset and thus M^{n+} ions are adsorbed onto the particle surface decreasing its negative charge. When the concentration of adsorbed ions $[M^{n+}] = [OH^-]$, we have the condition of Z.P.C. With increasing acidity more M^{n+} ions are adsorbed onto the particle and the latter assumes a positive charge.

Hydrophillic sols such as the oxides of silica, aluminium and iron obtain their charge due to hydrolysis of the surface of the sol particles. Healy (1968) considers that the surface of fragmented silica particles will have charged sites;

$$-\overset{|}{\underset{|}{Si}}^{+} \quad \text{and} \quad -\overset{|}{\underset{|}{Si}}-O^-$$

These sites are hydrolysed according to the following reactions;

$$-\overset{|}{\underset{|}{Si}}^{+} + H_2O \rightleftharpoons -\overset{|}{\underset{|}{Si}}-OH + H^+$$

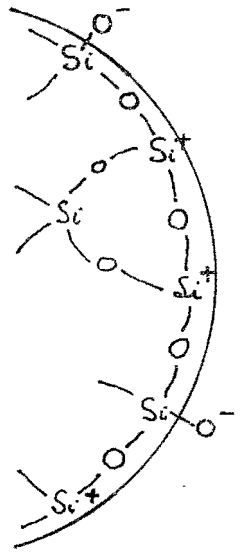
$$-\overset{|}{\underset{|}{Si}}-O^- + H_2O \rightleftharpoons -\overset{|}{\underset{|}{Si}}OH + OH^-$$

$$-\overset{|}{\underset{|}{Si}}OH + H_2O \rightleftharpoons -\overset{|}{\underset{|}{Si}}-OH_2^+ + OH^-$$

The ultimate charge on the silica particles will depend on the overall equilibrium.

$$-\overset{|}{\underset{|}{Si}}-O^- + 2H^+ \rightleftharpoons -\overset{|}{\underset{|}{Si}}-OH_2^+$$

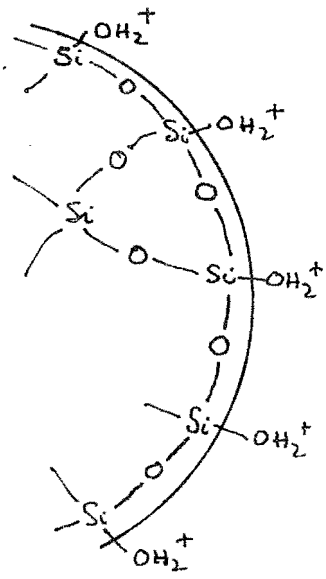
The equilibrium constant $Ke = \dfrac{[SiOH_2^+]}{[SiO^-]\,[H^+]^2}$



NEUTRAL SILICA FRAGMENT

H_2O

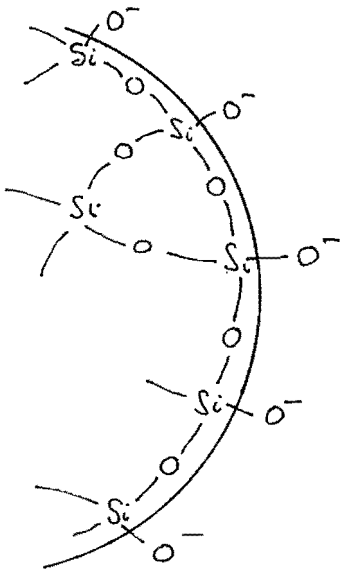
PH < 2·1



POSITIVE SURFACE CHARGE

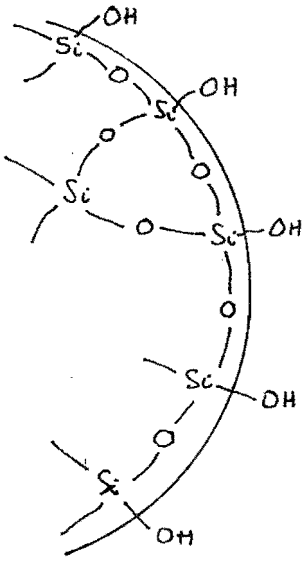
Z.P.C.

PH = 2·1



NEGATIVE SURFACE CHARGE

PH > 2·1



ZERO SURFACE CHARGE

Fig. 2 Diagrammatic representation of the charge on silica sol particles.

at the Z.P.C. $[SiOH_2^+] = [SiO^-]$;

then $Ke = \frac{1}{[H^+]}$ 2

and $pH = \frac{1}{2} \log Ke$

The above equation gives the pH at which the zero point of charge condition occurs.

Healy (1968) sites the following pH values at Z.P.C. for some common oxides.

Oxide	SiO_2	MnOOH	TiO_2	Fe_2O_3	Al_2O_3	MgO
pH at Z.P.C.	2.0	2	6.7	6-7	9.1	12

The value of pH at the Z.P.C. condition in a colloid system is very important, as it represents the pH at which all sol particles leave zero surface charge and are thus in their most unstable state.

4.2 The Electric Double Layer.

The particle charge in a colloidal sol system is always internally compensated by ionic species within the solvent. This produces what is referred to as the electric double layer. The inner layer of adsorbed ions which is commonly only mono-molecular consists of peptizing (stabilizing) ions while the outer diffuse layer consists of ions of opposite charge known as counter ions. Thus each sol particle is neutralized by a cloud of counter ions. Although the counter ions are electrostatically attracted to the oppositely charged surface there is a tendency for diffusion away from the surface into the dilute regions of the solvent. The cation and anion concentrations thus decrease away from the surface as shown in fig. 3. This ionic distribution is known as the Gouy Model of the electric double layer.

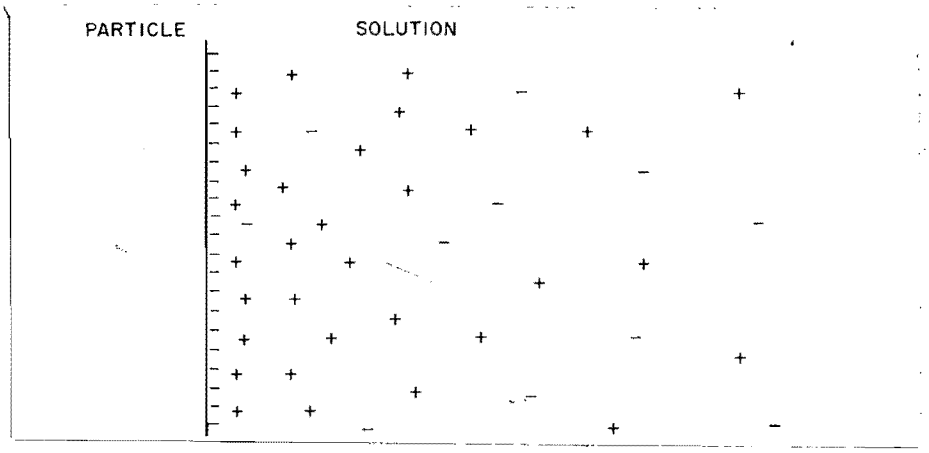


Fig. 3(a) Diffuse electric double layer model according to Gouy. (Olphen, 1966)

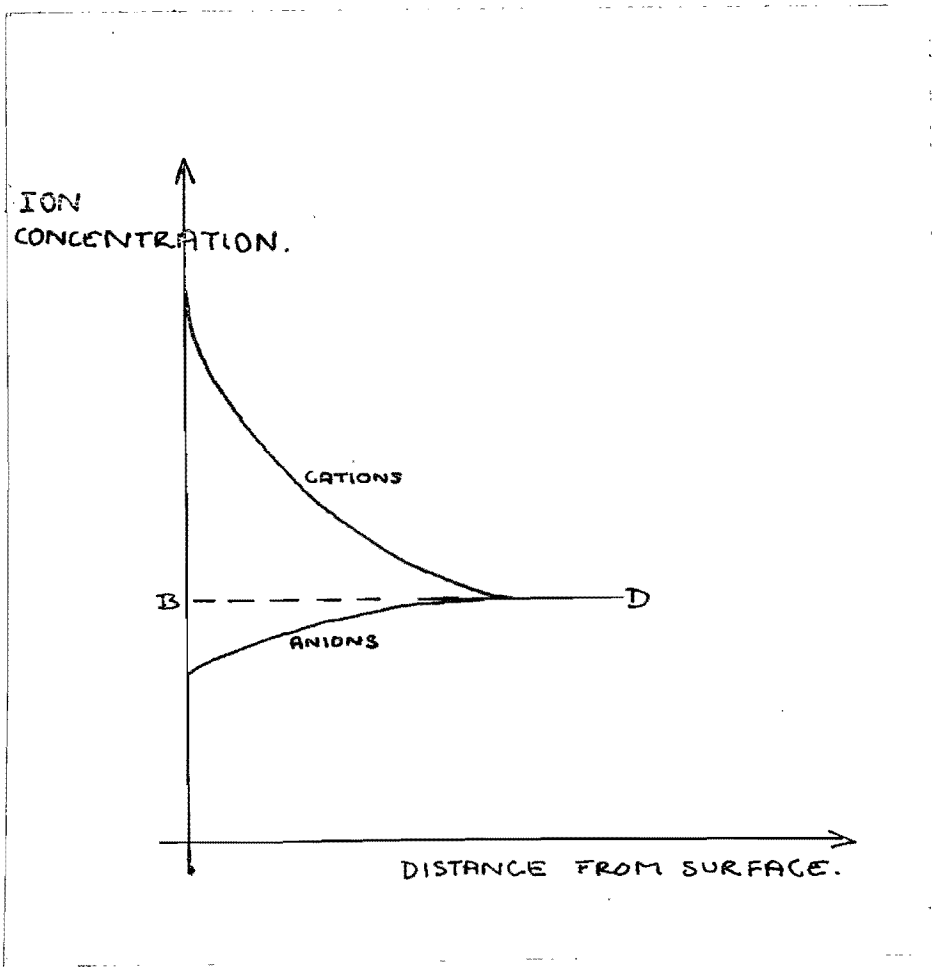


Fig. 3(b) Ion concentration as a function of distance from the surface, computed on the Gouy Model. (Olphen, 1966)

Olphen (1966) claims that if the double layer is created by the adsorption of potential determining ions only, the electric potential at the surface of each sol particle (ϕ_o) is given by the Nernst equation.

$$\phi_o = \frac{R\,T}{\nu\,F} \ln \frac{C}{Co} \qquad \text{Equ.1.}$$

Where ν = Valence of potential determining ions.

C = Concentration of these ions in solution.

Co = Concentration of ions when $\phi_o = 0$

F = Faradays number.

R = Universal gas constant.

Thus the concentration of ions in solution C, and the absolute temperature of the system T, are the only factors determining the electric potential at the particle surface. Computations using the Gouy Model show that the electric potential decreases from ϕ_o roughly exponentially with increased distance from the surface.

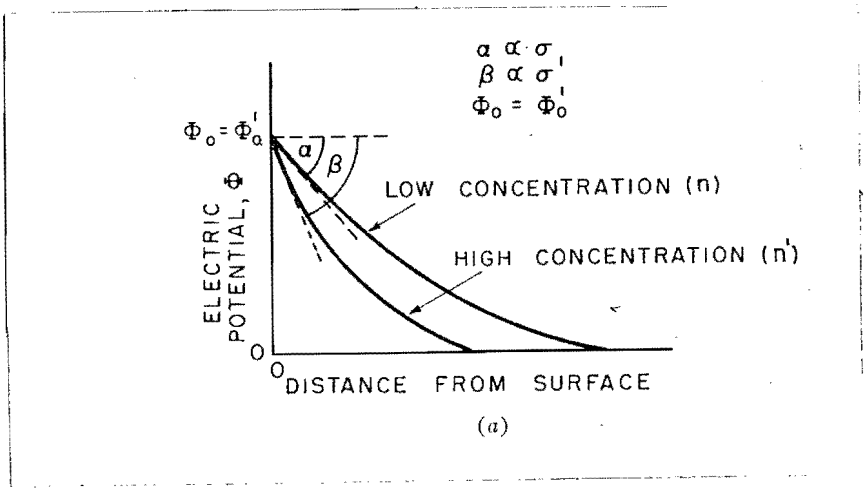
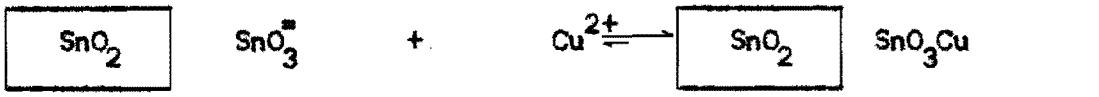


Fig.4. Electric potential distribution of diffuse double layer at constant surface potential for two electrolyte concentrations. (Olphen, 1966).

4,3 Coagulation in sol systems.

Interparticle attraction and repulsion forces operate simultaneously in a colloidal sol system, and the stability of the sol depends on their relative magnitude. Attraction is provided by van der Waals forces which act between atoms of different sol particles, while repulsion is between the similarly charged electric double layers surrounding each particle. With increasing concentration of dissociated ions in solution, the repulsive forces decrease while the van der Waals attraction remains constant. Thus, at high electrolyte concentrations, colloidal particles which collide due to random Brownian motion will stick together under the influence of the dominant attractive forces. Aggregates of colloidal particles thus grow out of the colloidal into the suspension size range, and settle out rather rapidly. Two theories have been promoted to account for the decrease in repulsive forces between electric double layers. (a) Discharge or neutralization of peptizing ions composing the inner layer of the electric double layer. (b) Compression of the electric double layer.

Jirgensons and Straumanis (1962) refer to electrophoretic experiments carried out by Freundlich which showed that for the arsenious sulphide (As_2S_3) sol, and the FeO(OH) sol, particle charge decreases with increasing electrolyte concentration. They thus conclude that discharging seems to be the cause of coagulation, but admit that the mechanism is not understood. The logical explanation is that electrolyte ions combine with peptizing ions to produce a neutral undissociated compound. This is exemplified in the coagulation of stannic acid by Cu^{2+} ions.



sol particle — Adsorbed peptizing ion — in solution — completely undissociated cupric stannate

Stannic acid is also coagulated by K^+ ions, but in this case the potassium stannate which results, completely dissociates in solution.

$$\boxed{SnO_2}\ SnO_3^{=} + 2K^+ \rightleftharpoons \boxed{SnO_2}\ SnO_3K_2$$

It is evident that the discharge theory is inadequate as it does not explain coagulation in all sol systems.

Cumputations using the Gouy Model show that the electric double layer is compressed when the bulk electrolyte concentration is increased. Olphen (1966) used Equ.1. and Equ.2. below, to calculate the "thickness" $(\frac{1}{K})$ of the electric double layer, for monovalent and divalent ions of various concentrations. (see fig.5).

$$\phi = \phi_o e^{-Kx} \qquad \text{Equ.2.}$$

where ϕ is the electric potential at a distance x from the particle surface.

APPROXIMATE "THICKNESS" OF THE ELECTRIC DOUBLE LAYER AS A FUNCTION OF ELECTROLYTE CONCENTRATION AT A CONSTANT SURFACE POTENTIAL

Concentration of ions of opposite charge to that of the particle, mole/liter	"Thickness" of the double layer, Å	
	Monovalent ions	Divalent ions
0.01	1000	500
1.0	100	50
100.	10	5

Fig. 5

It is important to note that the degree of compression of the double layer is only governed by the concentration and valence of ions of opposite sign to that of the surface particle charge.

The repulsion potential due to the interaction of electric double layers, and attraction potential due to the action of Van der Waals forces plotted as a function of interparticle distance for the one sol with three different electrolyte concentrations are shown in fig. 6.

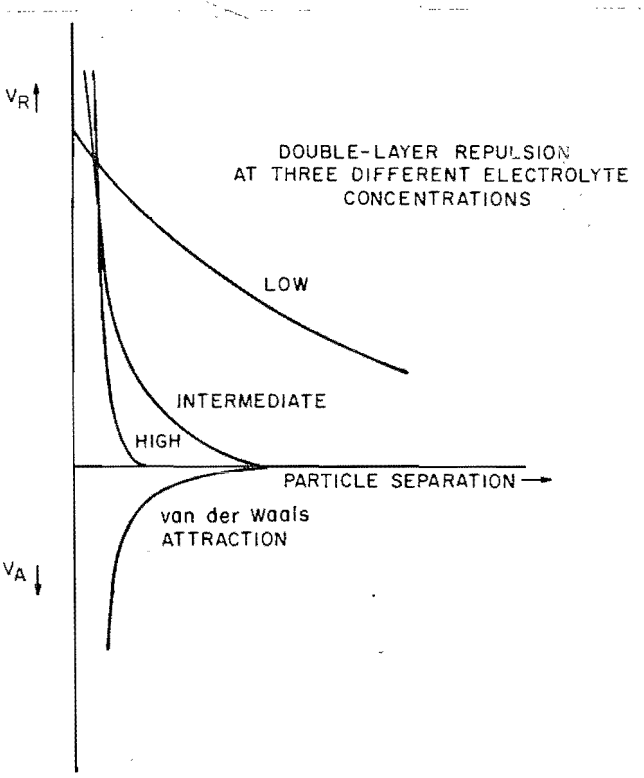


Fig. 6 Repulsive and attractive energy as a function of particle separation at three electrolyte concentrations.

Potential curves for each of the three electrolyte concentrations are produced by summation of the repulsive and attractive forces in each case. (Fig.7).

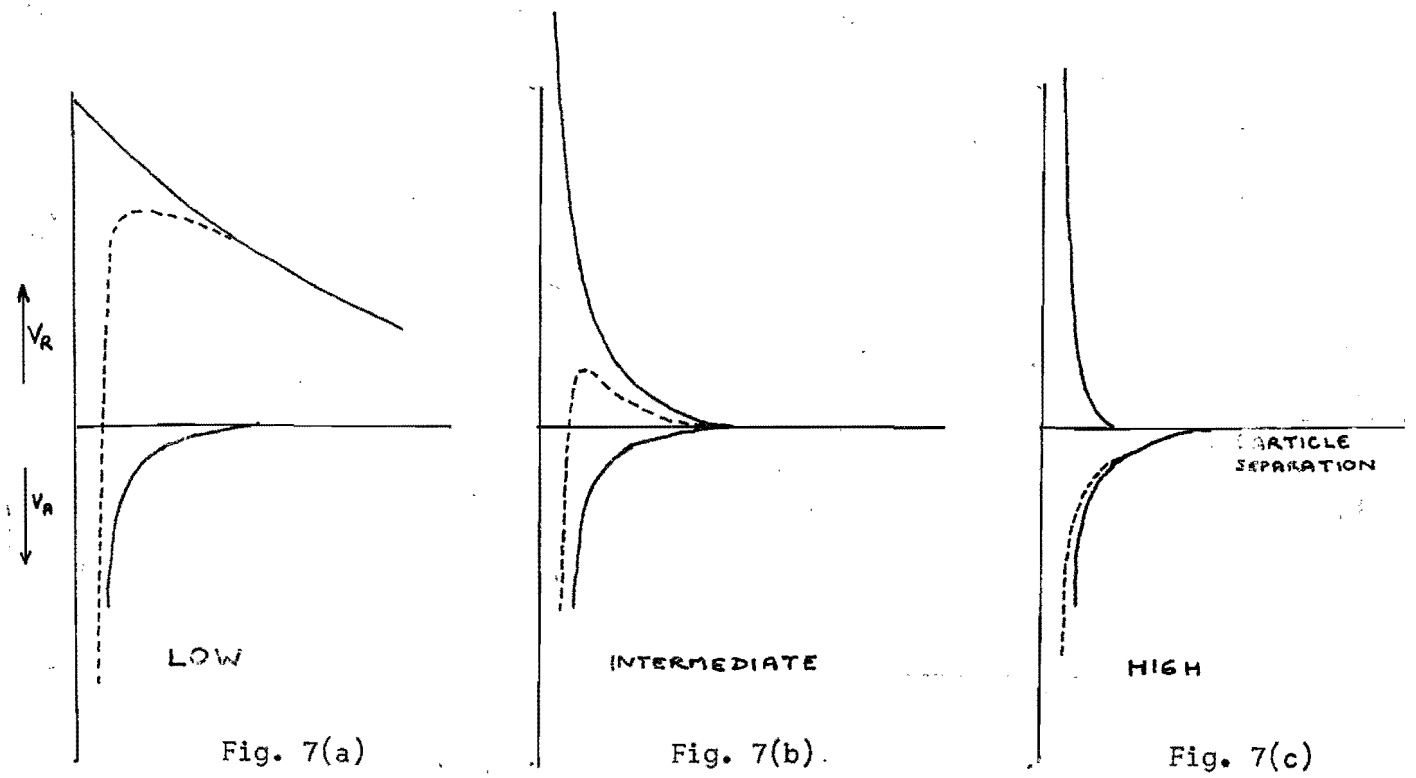


Fig. 7(a) Fig. 7(b) Fig. 7(c)

Net interaction as a function of particle separation.

At low electrolyte concentrations (fig.7a), most of the potential curve is above the distance ordinate and constitutes an "energy Barrier" to particle coagulation. Under such conditions the sol is said to be stable. At intermediate electrolyte concentrations (fig. 7b) the energy barrier has dropped and slow coagulation may proceed. At high electrolyte concentrations (fig. 7c) the potential curve shows attraction at all distances and coagulation occurs at the maximum rate.

When two compounds occur in the colloidal state within the one sol system, the process of coagulation is complicated by interaction between the different species present. Healy (1968) cites the SiO_2-Al_2O_3 sol system as a typical example. The variation of surface charge with ^{pH} for these two sols is given in fig. 8.

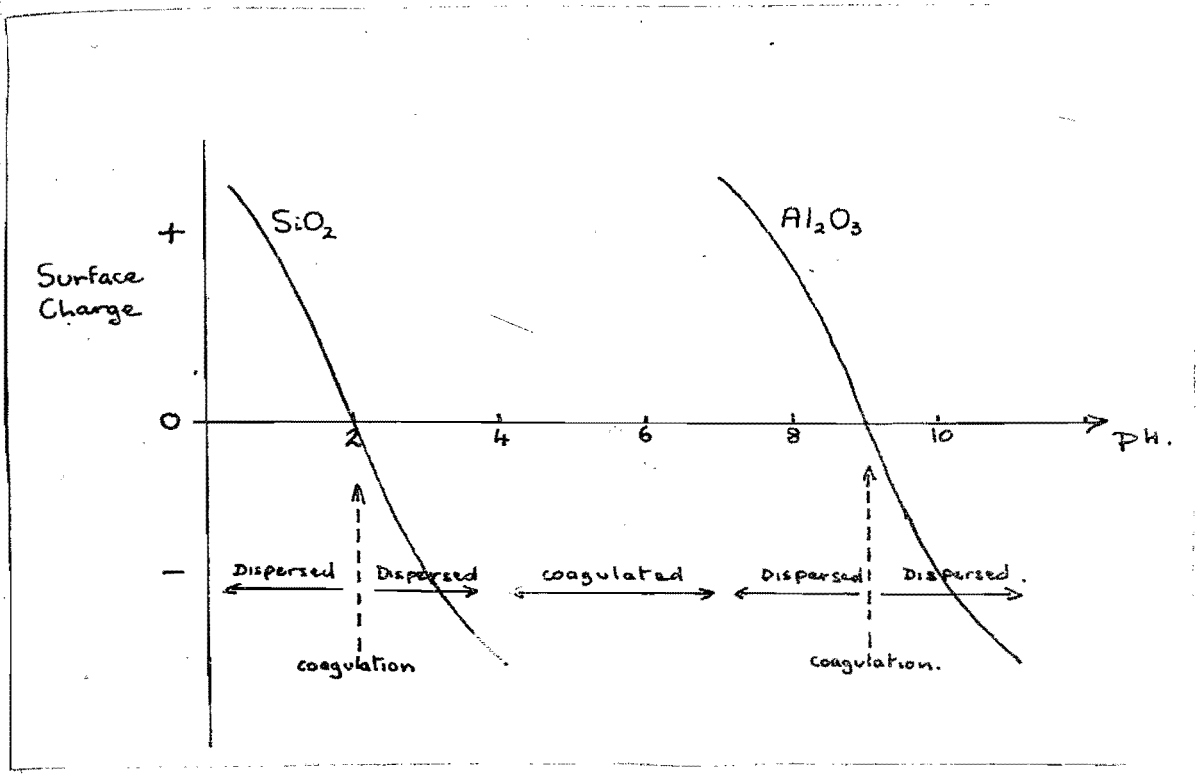


Fig. 8. Sol stability in the SiO_2-Al_2O_3 system.

Silica coagulates at its Z.P.C. of pH 2.0 and alumina coagulates at its Z.P.C. of pH 9.1. Between about pH 4 and 7 the silica particles have a negative surface charge while the alumina particles have a positive surface charge, and thus "mutual coagulation" occurs due to coulombic attraction. For pH < 2 and pH > 9.1 the dispersed sols are stable.

4.4 Coagulation power of electrolytes.

The coagulation power of an electrolyte acting on a particular sol is determined by its flocculation value*. Jirgensons and Straumanis (1962)

*Healy (1968) distinguishes flocculation from coagulation. He defines flocculation as an aggregation of colloids caused by polymeric species such as humic acids, tannins, and metal hydroxide polymers. He considers the polymer to link the sol particles forming large flocs which settle out. Due to the entrenchment of the term flocculation value in colloid literature, this term will be retained to avoid confusion.

define the flocculation value of an electrolyte as the minimum concentration of that electrolyte which is able to cause an observable decrease in the degree of dispersion of the sol under study. A list of flocculation values of some typical electrolytes is shown in fig. 9.

Fig. 9. Flocculation values of electrolytes for As_2S_3 sol containing 4·67 g As_2S_3 per litre

	*p*H	Flocculation values (millimol per litre)
LiCl	7·1	57·9
NaCl	7·1	52·9
KCl	7·1	48·6
RbCl	7·2	42·4
CsCl	7·0	29·1
NH_4Cl	6·3	38·5
HCl	1	34·5
$BeCl_2$	3·7	0·77
$MgCl_2$	6·2	0·90
$CaCl_2$	6·0	0·83
$SrCl_2$	6·0	0·80
$BaCl_2$	5·9	0·77
$AlCl_3$	5·7	0·085
$CeCl_3$	6·0	0·098
$LaCl_3$	6·0	0·088

It is evident from fig. 9. that the chief factor determining the flocculation value of a given electrolyte is the valency of the ion of opposite sign to that of the sol particles. Thus the ratio of flocculation power (reciprocal of flocculation value) for sodium chloride, magnesium chloride and aluminium chloride is;

$$NaCl : MgCl_2 : AlCl_3 = \frac{1}{52.9} : \frac{1}{0.9} : \frac{1}{0.085}$$

$$= 1 : 59 : 620$$

Computations using the Guoy Model for the electric double layer give flocculation values which approximately agree with observed values. This is one of the most important supporting factors for the Guoy Theory.

4.5 Adsorption of peptizing and counter ions.

Adsorption of ions in the inner peptizing layer and outer diffuse layer follow two separate processes.

(a) Ion exchange in the diffuse layer is determined by non specific adsorption, which is a simple ion adsorption controlled by the law of mass action. If A and B are two ions present in the sol system, then the equilibrium constant of adsorption may be defined as

$$K = \frac{[A]_i [B]_e}{[B]_i [A]_e}$$

where $[A]_i$ = activity of ion A in the diffuse layer

$[A]_e$ = activity of ion A in the equilibrium bulk solution.

For K = 1 both ions are adsorbed equally,

but K 1 implies ion A is adsorbed in preference to ion B. Non specific adsorption of ions does not effect the charge on the particle surface. Healy (1968) considers metal ions exchange for Na^+ ions on a negatively charged surface according to the following decreasing sequence;

$Fe^{3+} \gg Cr^{3+} > Al^{3+} > Ni^{2+} > Co^{2+} > Zn^{2+} = Cu^{2+} > Pb^{2+} >$
Group II ions $>$ Group I ions.

(b) Adsorption of ions in the inner layer is determined by specific adsorption in which there is a direct interaction between the ion and the surface layer. In this case the ions effect the charge on the particle surface and may adsorb onto a surface carrying a like charge. Healy (1968) proposes that specific adsorption obeys the relationship

$$G_{ads} = Z_+ e \quad (\psi_\delta - \phi_{chem})$$

where G_{ads} = free energy of adsorption.

Z_+ = valency of adsorbing ion.

e = electric charge on adsorbing ion.

Ψ_δ = potential at inner layer-diffuse layer boundary.

ϕ_{chem} = specific adsorption potential.

For Na^+, K^+, NH_4^+, Li^+ and Mg^{2+} the specific adsorption potential is zero. Specific adsorption onto silica at pH 5-6 shows the sequence of ϕ_{chem} values in the order;

$$Ca^{2+} < Ba^{2+} < Zn^{2+} < Co^{2+} = Ni^{2+} < Al^{3+} < Cr^{3+} \ll Fe^{3+}$$

A particular type of specific adsorption occurs when hydrolysable metal ions, inorganic and organic long chain polymers and complex ions adsorb onto colloidal surfaces. In aqeous solution iron and zinc ions may possibly adsorb as species of the type

$Fe(H_2O)_2(OH)_4^-$ and $Zn(H_2O)_6^{2+}$

4.6 Peptization and Protection of hydrophobic sols.

In the colloid literature peptization is used in two allied senses.

(a) A process of maintaining stability in a dispersed sol system.

(b) A process of bringing precipitated substances into the dispersed state.

It has been previously stated that repulsion of electric double layers between sol particles with strong surface charges maintains a stable system. These strong surface charges are provided by the peptizing ions of the inner double layer which are adsorbed onto the surface of the particles.

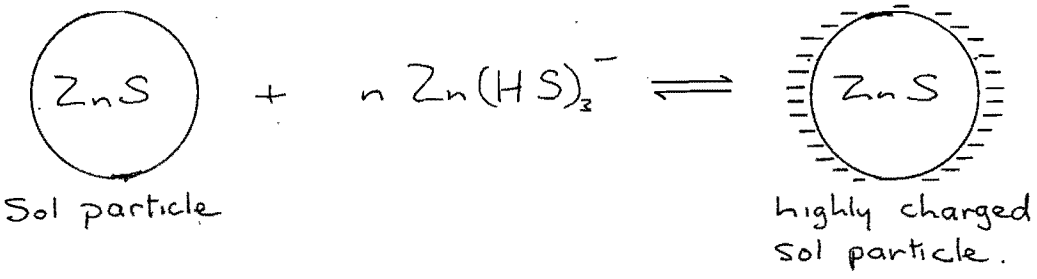
The adsorption of peptizing ions depends largely on the dissociation of ions in solution and consequently, in most cases on the pH of the system. Referring to fig. 1., it is evident that a negatively charged sol is peptized

by alkalies and a positively charged sol by acids. Hydrophobic sols such as silver iodide and barium sulphate may be peptized by their dissociated ions in solution, that is, a positive $BaSO_4$ sol is peptized by Ba^{2+} ions and a negative $BaSO_4$ sol by SO_4^{2-} ions.

It has been known for some time that insoluble metallic sulphides may be peptized by hydrogen sulphide or other soluble sulphides (Tolman and Clark, 1914; Clark and Menaul, 1916). The actual process involved has not been studied in detail. Due to the very low solubility of most metal sulphides, peptization by the sulphide ion ($S^{=}$) or the metal ion in the absence of H_2S, is out of the question. Jirgensons and Straumanis (1962) suggest that in the presence of hydrogen sulphide, metal complexes are formed which dissociate into ions, the latter being adsorbed onto the sulphide surface to produce highly charged and stable sols. In the case of zinc sulphide sols the bisulphide complex may be the important peptizing ion. Such ions are produced in alkaline conditions by the reaction;

$$ZnS_{(s)} + H_2S_{(g)} + HS^{-} \rightleftharpoons Zn(HS)_3^{-}$$

The negative $Zn(HS)_3^{-}$ ions are adsorbed onto the surface of the sol particles.



Strong negatively charged zinc sulphide sol particles result, which repel one another and form a stable dispension.

In highly alkaline environments, where the $S^{=}$ species predominates

As, Hg and Sb complex according as:

$$As_2S_3 + S^{=} \rightleftharpoons 2AsS_2^{-} \; ; \; K = 10^2$$

the high equilibrium constant means that the metal complex is highly dissociated and thus ions are readily available for adsorption.

Further development of this theory indicates that the degree of dispension of the metal sulphides will thus depend on;

(a) The stability of the complex metal sulphides formed.

(b) The extent of adsorption of the complex metal sulphide ion onto the surface of the particle (a function of type, concentration and temperature).

If we consider the second factor as constant, then the stability of sulphide sols peptized by hydrogen sulphide will parallel the equilibrium constants (K) for the most stable complexes.

In the chemical environment in which HS^{-} ions dominate ($7 \leq pH \leq 13$), Barnes (1967) cites the following K values.

	K
$HgS + H_2S + HS^{-} \rightleftharpoons Hg(HS)_3^{-}$	$10^{-3.5}$
$CuS + H_2S + HS^{-} \rightleftharpoons Cu(HS)_3^{-}$	$10^{-3.25}$
$ZnS + H_2S + HS^{-} \rightleftharpoons Zn(HS)_3^{-}$	10^{-3}
$CdS + H_2S + HS^{-} \rightleftharpoons Cd(HS)_3^{-}$	$10^{-2.69}$
$Sb_2S_3 + HS^{-} \rightleftharpoons HSb_2S_4^{-}$	$10^{-2.33}$
$Au + 2HS^{-} + \frac{1}{2}O_2 \rightleftharpoons 2AuS + H_2O$	$10^{29.7}$

Thus an increasing order of dispension of these sols in a mildly alkaline system, may be;

(Fe), Hg, Cu, Zn, Cd, Sb, Au.

Solubilities of iron bi-sulphide complexes are an order lower than those of copper and zinc (Barnes, 1967) and thus, iron would probably fit at

the front of the sequence. The order of such a stability sequence will vary according to the stable sulphur species present in the system (H_2S; HS^- or $S^=$) and thus on the pH of the system. Insufficient data on complex formation is at present available to place any emphasis on the sequence above.

A second process of stabilization of hydrophobic sols, involves protection rather than peptization. In this case the stabilization occurs due to the presence of a hydrophillic colloid in the system. Olphen (1966) states that this process considerably increases the flocculation value of the hydrophobic sol, even to such an extent that the sol may remain stable in concentrated salt solutions.

Jirgensons and Straumanis (1962) note that gelatin protects silver colloids against coagulation by sodium chloride. Silica forms a typical hydrophillic sol, and has been observed to have a protective action over hydrophobic sols. Bastin (1950) used a silica sol to disperse gold and silver sols in solutions containingchalcocite and chalcopyrite. In the abeence of silica sol, the gold and silver were precipitated by the ore minerals. This protective action of silica may be very important in stabilizing hydrosols in a hydrothermal ore fluid.

This mechanism of stabilization by hydrophillic colloids is little understood. However most authors agree that the hydrophillic colloid probably envelops hydrophobic sol particles, by the development of a monomolecular layer over the whole surface. The hydrophobic sol thus assumes the surface properties of a hydrophillic sol, i.e., increased stability and high salt resistance.

5. GEL SYSTEMS

Coagulation of concentrated colloidal sols commonly leads to the formation of a gel. In the gel, the particles are linked together to form a continuous coherent framework which extends throughout the volume. The solvent inter-penetrates the gel network, which is very open and capable of holding high concentrations of ions.

5.1 Formation of gels.

Jirgensons and Straumanis (1962) describe four methods by which gels may be formed.

(a) Coagulation of sols or decrease in solubility of the solution.

(b) Chemical reaction between two concentrated true solutions.

(c) Gelation of hydrophillic sols on cooling.

(d) Swelling of xerogels.

The first two methods are those of most importance in geological environments.

The production of gels due to coagulation of colloidal sols is promoted by three factors; (i) A high degree of linearity of the sol particles, (ii) high concentrations of sol, and (iii) increased solvation of the particles. Arsenious sulphide, sulphur and gold, which form spherical sol particles do not form gels. This is logical when it is realized that asymmetric particles more easily build up a network capable of immobilizing the solvent, than symmetric particles.

Gels are formed in chemical reactions of concentrated solutions (method b) if one product of the reaction is insoluble, and if the particles tend to form linear aggregates. Lebedev (1967) produced zinc sulphide gels by adding highly concentrated sodium sulphide solution to variously concentrated solutions of zinc sulphate.

$$Na_2S + ZnSO_4 \longrightarrow \underset{gel}{ZnS} + Na_2SO_4$$

5.2 Structure of gels.

Structurally, gels have been divided by Jirgensons and Straumanis (1962) into three separate groups.

(a) Gels with unstable networks, such as ferric hydroxide, aluminium hydroxide, bentonite and graphite, in which the particles are joined by weak van der Waals forces which are often destroyed by shaking, but re-form on settling. Such gels are denoted thixotropic.

(b) Gels with metastable networks where hydrogen bonds form the import- and linkages between particle units. This group constitutes the proteins and is not important geologically.

(c) Gels with stable networks where the bonds between particle units are similar to those within the units. Silica gel is a typical example of this type.

5.3 Ageing and Crystallization in gels.

The term ageing denotes spontaneous changes taking place within the gel. Thermodynamically gels are unstable, and given time, must crystallize to the more stable form. In general the crystallization involves a rearrangement of the bonds within the random amorphous structure of the gel to form an ordered crystal lattice. This is accompanied by expulsion of the inter-mixed solvent. The progress of crystallization in the gel is best studied from X-ray powder patterns taken at successive intervals during the ageing. Chukhrov (1965) refers to experimental work by Durov and Drobysheva (1959) who found that a chalcopyrite gel initially exhibiting very poor crystallization yields a far clearer X-ray powder pattern after three and one half months ageing at room temperature. Lebedev (1967) aged zinc sulphide gels for a period of up to twelve months. After six months, the major part of the gel

was completely amorphous, while after twelve months, five wide but distinct sphalerite lines were evident. He found that the rate of crystallization was markedly affected by the temperature of the system and the concentration of electrolyte ions in the solvent. These experiments are discussed in more detail in section 7.2

Crystallization in gels is accompanied by a spontaneous process of dehydration with associated decrease in volume. This phenomena is known as syneresis. Syneretic cracks commonly develop in the gel, these may be radial, parallel to compositional banding,or irregular. Kruyt (1949, Vol 11) points out that the influence of concentration, temperature and the addition of salts, on syneresis, may be rather complex.

5.4 Silica gel.

Silica gel is the most important gel system in geological environments and thus a clear understanding of its formation and structure is necessary. Basically the gel is produced by the polymerization of silicic acid in a low pH solution. The theory established by Carman (1940) appears to be accepted by most workers in this field. He considers the gelation to take place in two stages. These are the first two steps represented in fig.10. Initially the silicic acid molecules, $Si(OH)_4$, condense to form polymeric silica particles which constitute a sol. The particles are hydrolysed on their outer surface and dispersed by the like negative surface charge. When the sol concentration exceeds about one percent silica, the polymeric particles become linked together via Si-O-Si bonds to form linear and space polymeric units which constitute the continuous open gel framework. Due to the shape of the silica sol particles, the number of Si-O-Si links between particles is less than the number within them. Unsatified sites of the $-\overset{|}{\underset{|}{Si}}-O^-$ and $-\overset{|}{\underset{|}{Si}}-OH_2^+$

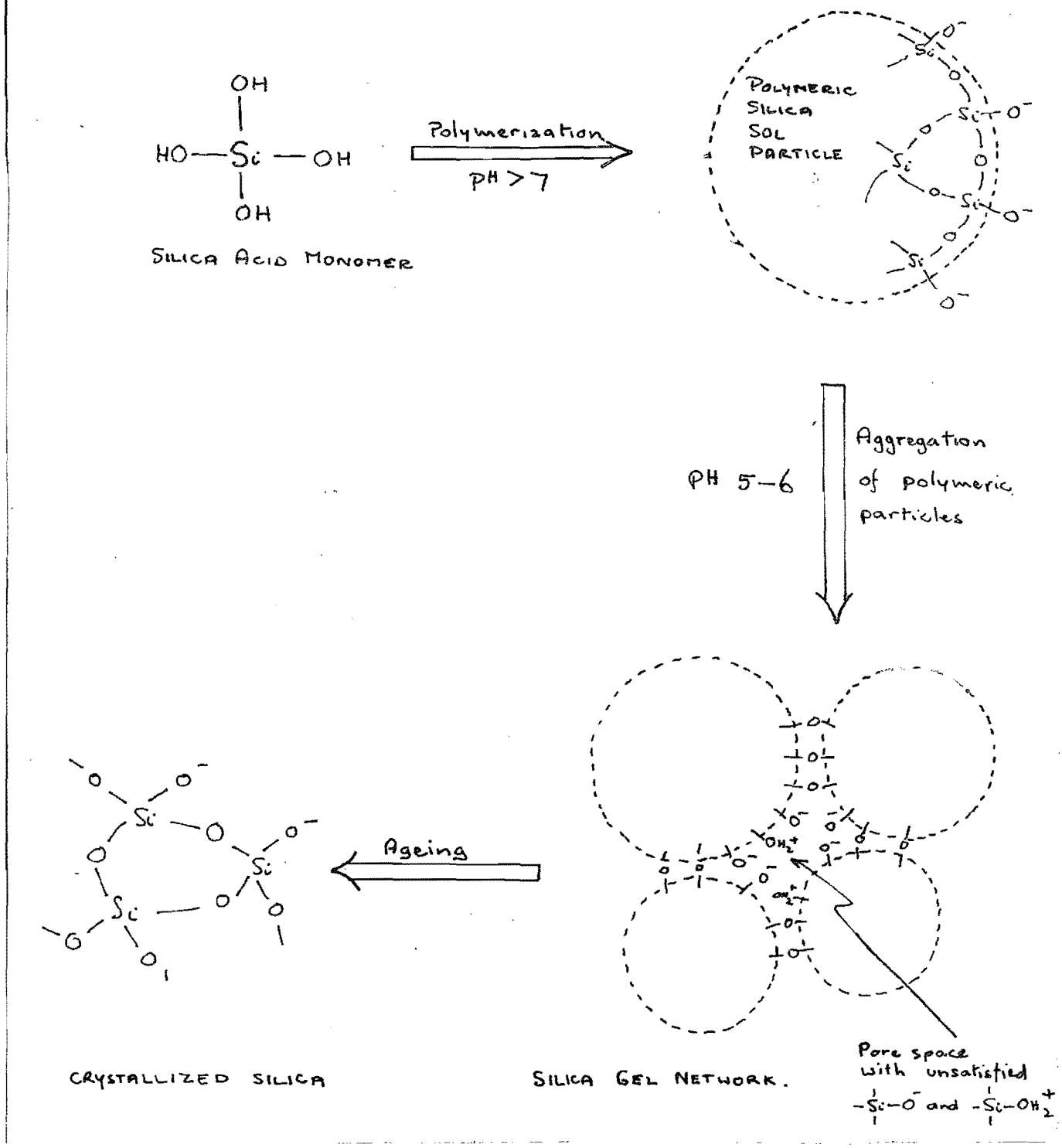


Fig. 10 Formation and ageing of silica gel.

type thus exist in pore spaces within the network. Healy (1968) considers that the high dielectric constant of water is an important factor in the stabilization of these unsatisfied sites. A third stage which encompasses crystallization may be added to Carman's bi-stage process. This involves rejection of water from the structure, promoting instability of internally charged sites. Stability is attained by a gradual rearrangement of bonds in such a way that the disordered Si - O - Si networds form into systematic tetrahedral SiO_4^{4-} units which constitute a crystal lattice.

Healy (1968) reports on recent unreferenced work by Hazel who considers that the formation of Si-O-Si linkages in the gelation process is influenced by the following factors:

(a) The proportion of Si-OH to $Si-O^-$ groups, the concentration of the latter increasing with increased pH.

(b) The concentration of silicate.

(c) The large activation energy involved in forming the activated complex form Si-O and O-H.

(d) The entropy or geometrical factor associated with forming the activated complex, the precursor to the covalent linkage.

The effect of pH on gelation is fully discussed by Iler (1955). This is summarised in fig. 11.

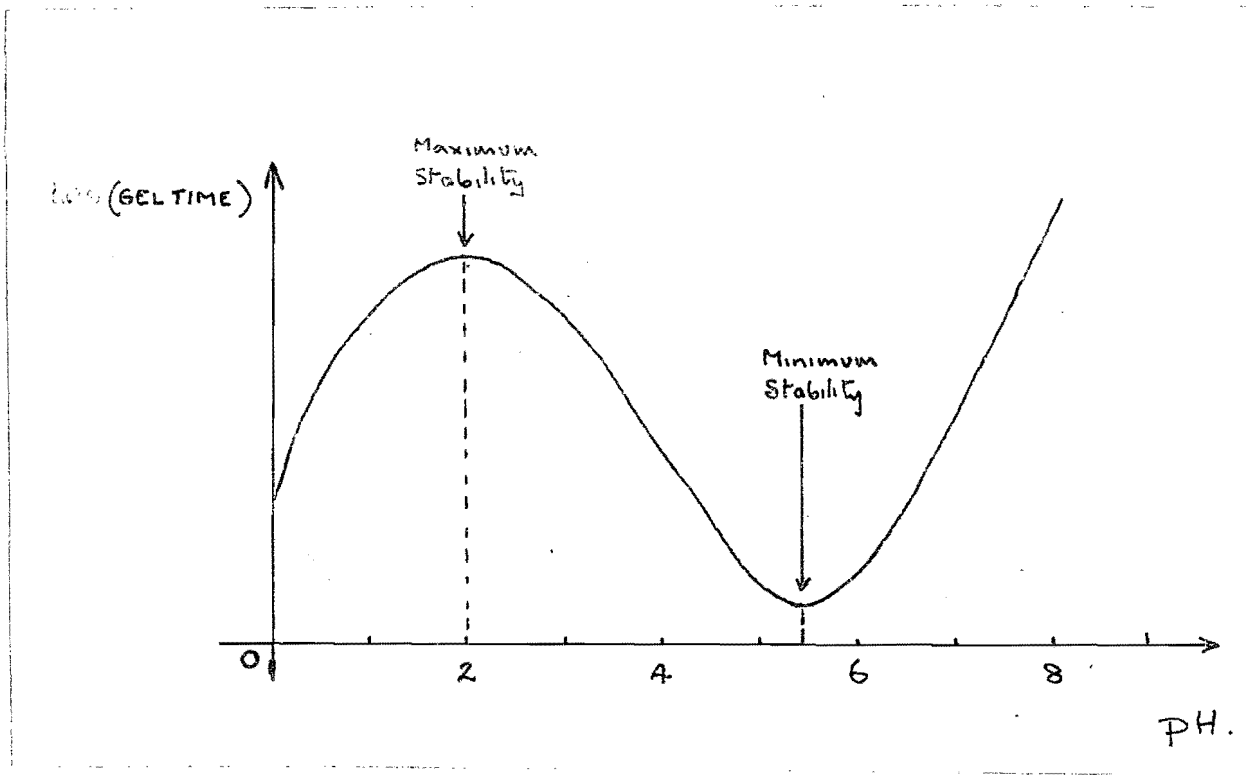


Fig.11. Silica sol stability as a function of pH (Iler, 1955).

For alkaline solutions of pH 7, provided electrolytes are absent from the solution, the silica sol particles bear a strong negative charge and remain in a dispersed state. The formation of Si-O-Si linkages between sol particles is best promoted between pH 5 to 6. Rapid gelling results under these conditions. The sol shows maximum stability at about pH2. This seems contradictory as the zero point of charge of a silica sol accurs at pH2 also. Iler considers that although the sol particles are unchanged, polymerization cannot occur due to the absence of OH^- ions, which tend to catalyse the condensation reaction. At pH 2 the gelation rate is proportional to the concentration of H^+ ions and F^- ions. Healy (1968) considers that highly anionic species such as metal hydroxy- or metal chloro- complexes may be more important than F^- ions in geological environments (sedimentary piles).

6. TEXTURES OF COLLOIDAL PRECIPITATES.

The textures of ore minerals may give some indication to the mechanism of precipitation, from the ore forming fluid, but do not supply any evidence on the method of transport of the metal ions within the fluid. Thus, a particular texture may supply strong evidence for the crystallization of a mineral from a gel system but no evidence as to whether the mineral was transported as a sol or in true solution. Many workers (including Lasky (1930) and Rust (1935)) who have observed ore textures which suggest the precipitate passed through a gel stage automatically concluded that the minerals were transported as the dispersed sol. Such an inference is unfounded as gels may equally develop from true solutions.

6.1 Surface tension effects.

Textures resulting from surface tension effects may be grouped under the term "colloform", and include; globular, framboidal, oolitic and reniform (botryoidal).

(a) Globular; Experimental work by Lebedev (1967) on zinc sulphide and lead sulphide gels indicates that spherical globules begin developing immediately after the gel coagulates. The globules are generally only evident under the highest magnifications of an optical microscope but are the initial stage in the formation of macroscopic colloform textures. Lebedev (1967) reports having studied globular textures in the following minerals; vein quartz, hydrohematite, cassiterite, sphalerite, pyrite, opal and silica deposited from hot springs.

(b) Framboidal; Coalescence of globules due to subsequent diagenesis and ageing of the gel will produce globulites or framboids (Lebedev, 1967).

The typical example is framboidal pyrite of sedimentary environments. Sphalerite, chalcopyrite, cassiterite and crystobalite have been recorded by other workers (Schneiderholn, 1923; Lebedev, 1967; Rust, 1935). The globules may be orderly or disorderly arranged throughout the framboid. Love (1966) describes four patterns of ordering within pyrite framboids, which include, square, hexagonal and irregular to six-sided. Schneiderholn (1923) considers that chalcopyrite framboids in the Kupferschiefer, Germany, developed from gels which coagulated due to the action of biogenic H_2S on the metal ions in solution. This theory is supported by the work of Love (1964) who has demonstrated that the framboidal sulphides of the Kupferschiefer, Rammelsberg and Mt. Isa ore deposits all contain interstitial organic material. This may be significant although he points out that such organic material is mostly absent from pyrite spheres of recent sediments. Healy (1968) suggests organic polymeric material may play an important part in the development of framboidal textures in bacterial environments. The organic polymers arrest crystal growth of submicroscopic FeS nucleii and flocculate the nucleii into aggregates by a bridging process. This would account for the interstitial organic material observed by Love (1964). Bastin (1950) cites Schouten (1946) who reports framboidal textures from (i) the Cornwall Mine, Missouri, (ii) the Rio Tinto Mine, Spain, and (iii) the Redpath Mine in Cornwall. Schouten rejects a bacterial-gel origin due to "the undoubted hypogene" nature of these deposits. It is the writer's opinion that a bacterial-gel origin for framboidal sulphides should only be proposed when there exists good evidence for a depositional environment which favours bacterial development.

(c) Oolitic: Oolites are spherical mineral aggregates with a concentrically zoned internal structure. When the size exceeds two millimeters

in diameter, the term pisolites is used. The concentric zoning may be of depositional or diffusional character. An oolitic texture is not characteristic of a primary gel phase, as they may easily form due to successive crystallization from true solution (Edwards, 1947).

(d) Reniform: The reniform or botryoidal structure encompasses mineral aggregates with hemispherically uneven surfaces, commonly in the macroscopic size range. Most reniform minerals exhibit banding that parallels the curved external shape, and a radial acicular crystal structure approximately normal to the banding. In a detailed analysis, Lebedev (1967, pp. 43-50) concludes that reniform textures may result from either crystallization in true solutions, or ageing in gel systems. He distinguishes three separate types:

(i) Coagulative-diagenetic reniform aggregates: The coalescence of globules in a globulated gel is gradually dampened during thickening of the gel. The result is an aggregate of semi-coalescent globules, which possesses a reniform appearance. Lebedev produced hemispheroidal units of zinc sulphide gels with diameters up to eight millimeters.

(ii) Crust type reniform aggregates which are divided into two groups: (I) those resulting from rythmic coagulation of a sol onto a surface, (II) deposits on a surface precipitating from true solutions flowing past the surface. The latter type may be distinguished by asymmetry of the aggregates, due to the solution flow from one constant direction.

(iii) Reniform aggregates of crystallization type: These result from mutual interaction of individual spherulites* crystallizing from a true solution. Lebedev maintains that the reniform textures of the crystallization

*Spherulites are spherical mineral aggregates with a radiating crystal structure.

type are distinguished from those of gel origin by the fact that spherulites in the former show mutual interpenetrate contacts while those in the latter develop flat contact surfaces.

Chukhrov (1965) cites a number of Russian authors who consider that all reniform textures with a radiating internal crystal structure result from crystallization in true solutions. He maintains that this is possible for smooth surfaced reniform masses of ore minerals if the following ideal conditions were to be observed.

(i) Strict simultaneity in development of the crystallization centres.

(ii) Their appearance on an idealy smooth surface.

(iii) Absolute uniform supply of solutions to all parts of the growing aggregate.

As these conditions are not upheld in nature, Chukhrov concludes that such reniform textures cannot have crystallized from the solution, but must be indicative of gel formation.

It is generally accepted that the colloform textures described above develop due to surface tension effects in the gel. Because of the low viscosity of unaged colloidal gels, surface tension operates to produce the smallest surface area per unit volume. The limit of this process is the production of spheres or globules. Globulation about a number of centres in the gel network thus results in a reniform structure. Alternatively stated, the spherical shape is produced due to the excess free surface energy at the boundary between the two phases (gel and solution).

Roedder (1968) disputes the effect of surface tension in producing colloform aggregates. He considers that the typically colloform sphalerite of the Pine Point deposit in Canada crystallized directly from the ore fluid

and not from a gel. Roedder maintains that above a certain yield stress thixotropic gels "flow as liquids". Thus, if the surface tension forces exceed this stress, spherical forms cannot develop within the gel. Roedder then states "However, the curved mammillary or reniform surfaces of 'colloform' minerals exhibit a very wide range of radii, even for the same layer". A major fault in this argument is evident when it is realised that silica gel, which commonly develops colloform textures in opal, chalcedony and vein quartz, is not thixotropic but a very stable gel.

6.2 Liesegang Ring development.

Colour banding within mineral aggregates exhibiting colloform textures is very common. The bands are generally concentric with the outer surface of the mineral and may vary considerably in thickness. In colloform sphalerite the macroscopic banding varies from white through yellowish brown to very dark reddish brown (Roedder, 1968), and is mostly due to the different iron content of zinc sulphide within each band. Under high magnification, Roedder reports that very fine colour banding is caused by a variation in grain size of the individual bands.

Proponents of a gel origin for colloform textures propose that such banding is produced by Liesegang ring development previous to crystallization of the gel. This process provides a method of producing periodic precipitation within a gel. It involves the diffusion of ions from the surface into the gel network, with periodic precipitation produced by complementary ions dissolved in the interstitial solvent. Healy (1968) describes a simple experiment in which sulphide ions were slowly diffused through silica gel in which lead nitrate had been dispersed. Lead sulphide precipitated in clearly demarked bands, and crystallized to form near perfect cubes. Healy claims

that, in a static isothermal system, with constant precipitant ion concentration, the spacing between the bands conforms to a geometrical progression. $\frac{X_n}{X_{n+1}}$ = Constant; Where X_n is the distance of the nth layer from the gel surface.

Variations in (i) temperature, (ii) salinity of the solution, (iii) concentration of the precipitating ion, and (iv) the composition of the interstitial fluid, will cause variation in the composition of the bands and the spacing between them.

Previously cited theory (section 5.4) indicates that the interstitial pore fluids of an ageing silica gel contain high concentrations of OH^- ions. Thus Al^{3+} or Fe^{3+} ions present in the depositing solutions which diffuse into the gel network may be precipitated periodically as $Al(OH)_3$ or $Fe(OH)_3$. Such a process may account for bands in agate which are coloured due to iron and aluminium impurities in the silica. A similar mechanism can account for the iron rich bands developed in colloform sphalerite. If the zinc sulphide gel coagulates from a zinc sulphide sol, then the peptizing ions will pass into the interstitial fluid. This fluid will thus be enriched in ions of the type $Zn(HS)_3^-$. Fe^{2+} ions diffusing from the outer surface into the gel will thus be deposited periodically as (Fe, Zn)S.

Roedder (1968) considers that the internal banding evident in colloform sphalerite from the Pine Point deposit, resulted from periodic changes in the fluids from which the zinc sulphide was crystallizing. He suggests that these periodic changes may be annual and thus describes them as "varves". Roedder (1968) notes that under high optical power many of the colour bands are controlled by sig-zag boundaries. He claims that this

precludes any diffusion process as the mechanism of development for the bands. Roedder will not accept the fact that crystallization during ageing of the gel, and subsequent to development of Leisegang bands, is the most probable cause for these zig-zag boundaries. Edwards (1947), and many others, consider that an important criteria for gel development is provided when an individual acicular radiating crystal is observed to pass through more than one band in colloform banded minerals. It is hard to imagine how this situation would develop due to crystallization from true solutions. Roedder (1968) also disputes the idea that crystallization of a gel initially takes place at the centre and radiates outwards. Healy (1969b) points out ".....he (Roedder) fails to understand that concretionary growth, sol coagulation or flocculation or gel collapse is most pronounced in the centre (i.e., the original matter) of the unit. Sol to crystal, or gel to crystal, is most likely to begin in the centre."

6.3 Syneresis Cracks.

Syneresis cracks which develop as the gel rejects its interstitial fluid and begins crystallizing are commonly preserved in colloform aggregates. The cracks may be filled with other minerals, for example, galena filling cracks in colloform sphalerite. An irregular network of cracks is the general development, but radial and concentric cracks may also form. Roedder (1968) claims that cracks of this type, developed in colloform textures cannot be considered as a criteria for gel origin. He maintains that most gels contain from 50 to 90 percent water and hence would be expected to contract from 50 to 90 percent by volume on crystallization. However, the sphalerite samples examined indicate little shrinkage at all. Healy (1969b) counters this argument by indicating that in nature gels are open systems and thus ions or

sol particles may be deposited in the pores of the gel from fluids moving through the network. It follows that contraction on crystallization will be considerably reduced.

It is evident from the above discussion that an original gel stage in the deposition of ore minerals is only indicated by relicts of textures and structures. Subsequent crystallization generally destroys the most characteristic structures of the gel. Thus mineral aggregates deposited from a colloidal system need not necessarily show colloform textures, and indeed a sol stage cannot be inferred from colloform textures.

7. EXPERIMENTAL WORK ON COLLOID SYSTEMS IN ORE TRANSPORT AND DEPOSITION.

Experimental work in this field, previous to 1950 has been restricted to simple laboratory experiments studying the stability of colloidal systems (especially sulphide sols) in low temperature, pressure environments. In recent years Russian researchers have completely monopolized the field, but unfortunately only a small portion of their published literature is available to the writer. The following summary of experimental work is thus not all-encompassing, but at least indicates the trends in research in the field.

7.1 Sulphide sols.

Tolman and Clark (1914) studied the peptizing action of hydrogen sulphide on the copper sulphides, covellite, chalcopyrite, bornite and chalcocite. They found that in alkaline solution hydrogen sulphide dispersed the sulphide sols according to the sequence;

Chalcocite > covellite > bornite > chalcopyrite.

Dispersion in acid solution was to a lesser degree, but the same sequence was observed. The theory of sulphide dispersion by hydrogen sulphide, discussed in section 4.6, indicates that the sol particles generally acquire a negative surface charge, that is, the Z.P.C. occurs at a very low pH. This accounts for the observation that the copper sulphides are better peptized in alkaline solutions.

The peptizing action of hydrogen sulphide on copper sulphides was found by Tolman and Clark to be increased by the presence of NaCl or KCl in solution, but decreased by $CaCl_2$, $CaCO_3$, $AlCl_3$ and Al_2O_3. The presence of Al_2O_3 coagulated the sols very rapidly. The writer cannot account for this apparent peptizing action of NaCl, which is contrary to the usual coagulating

action of electrolytes in solution. But, nevertheless, this is a very important piece of experimental data which supports the fact that colloidal sulphide sols are stable in ore fluids rich in brines. The strong coagulating power of Al_2O_3 may result from the process of mutual coagulation (see section 4.3). The Z.P.C. of Al_2O_3 sols occurs at pH 9.1 (Healy, 1968), thus in mildly alkaline and acid solutions Al_2O_3 particles possess a positive charge while sulphide sol particles possess a negative charge

For the mechanism of coagulation by $CaCO_3$, Rust (1935) considers the action of hydrogen sulphide produces a soluble coagulating electrolyte.

$$2CaCO_3 + 2H_2S \rightleftharpoons Ca(HS)_2 + Ca(HCO_3)_2$$

The hydrosulphide and bicarbonate are both soluble enough to act as coagulating agents. This reaction produces a double barrelled cause for coagulation; (i) Removal of the peptizing agent, hydrogen sulphide. (ii) Production of two effective coagulating agents.

Tolman and Clark also found that CO_2 caused increased dispersion of the copper sulphides in the presence of hydrogen sulphide, but coagulation in the absence of hydrogen sulphide. It was observed that with increasing temperatures up to 200° C the peptizing action of H_2S was increased.

Clark and Menaul (1916) carried out similar experiments in which they studied the peptization of the following sulphides by H_2S; pyrite, pyrrhotite, arsenopyrite, sphalerite, covellite, bornite, cobaltite, cinnabar, stannite, enangite, tetrahedrite, stibnite, argentite, smaltite, orpiment, prouslite and realgar. Hydrogen sulphide was passed through alkaline solutions containing the finely powdered sulphides and after two months and seven days, each solution was tested quantitatively for the respective minerals. All the sulphides except argentite and proustite became dispersed in solution, with

concentrations ranging from 2% (pyrrhotite) up to 30% (stannite). Limestone and alumina suspended in the peptized sols caused partial coagulation, while at the same time some of the limestone passed into solution.

It is important to note that in no section of the papers by Tolman and Clark (1914) or Clark and Menaul (1916) is it stated that the peptized sulphides were tested optically to prove existence in the colloidal sol state. Macroscopic evidence may have suggested a sol condition, but this is not stated.

Kania (1936) studied the transport and deposition of silica, pyrite, chalcopyrite and sphalerite from sols dispersed by sodium sulphide and charged with hydrogen sulphide and/or carbon dioxide. Throughout his paper Kania mixes his terms "solution" and "sol", and in many cases it becomes very difficult to interpret his results. A typical example is page 460, where he infers that a mixture of Na_2S - FeS_2 in water forms an aqueous solution. According to Barnes (1967), iron does not form appreciably soluble complexes with H_2S, HS^- or $S^=$ up to temperatures of 200° C. It thus appears more probable that the Na_2S is acting as a peptizer to the FeS_2 sol, rather than the formation of a soluble double sulphide. An important observation by Kania was that siliceous rocks have a peptizing effect on FeS_2 and ZnS sols. This is possibly explained by the protective action of the hydrophillic silica sol on any hydrophobic sols.

Generally his experiments showed that Na_2S-SiO_2 "solutions" coagulated FeS_2 sols which in turn coagulated $CuFeS_2$ and ZnS sols, in that order. Assuming the ore fluids containing these metals were derived from a deep magnetic source, then Kania concluded that their order of ascent would depend on the dispersion sequence established in the experiments; i.e., silica (first), followed by pyrite, chalcopyrite and sphalerite.

Kania maintains that rising SiO_2-Na_2S "solutions" charged with H_2S and CO_2 will release their CO_2 and H_2S due to decreasing pressures. Na^+ ions pass into true solution as bicarbonate and coagulate the SiO_2. Subsequent intrusion of Na_2S-FeS_2 "solutions" result in the dispersion of previously deposited SiO_2 and the coagulation of FeS_2. The dispersed silica is carried upwards and deposited as a second generation. In turn chalcopyrite and then sphalerite replace FeS_2 and SiO_2 with the replaced mineral being carried further along the path of the ascending solution. Such a mechanism gives rise to the following paragenetic and zoning sequence; silica (first, and furthest from source), pyrite, chalcopyrite, sphalerite. Kania considers this sequence to be observed in the following deposits;

(i) Jerome, Arizone, (ii) Rio Tinto, Spain, (iii) Hidden Creek Mine, Anyox, B.C., and (iv) Mount Lyell, Tasmania.

It appears to the writer that this mechanism for transport and deposition of the sulphides studied, is based on too little experimental fact and no physico-chemical theory.

Chukhrov (1965) discusses experimental work by Lopatina, Losev and Smurov (1960) who studied colloidal sols of PbS, ZnS, CuS and FeS_2 peptized by H_2S up to temperatures of 250° C. They found that the stability of the sulphide sols depended on the combinations present, and that in some cases (including sols of PbS and PbS + FeS) hydrogen sulphide had no stabilizing effect. Contrary to the results of Tolman and Clark (1914), Lopertinal et al. observed that the dispersion of the sulphide sols decreased with increasing temperature. They give the following overall concentrations of metal in stable sols;

(1) 300 mg l^{-1} at temperatures up to 150 - 170° C.

(2) 40 - 60 mg l^{-1} at temperatures up to 250° C.

Chukhrov comments, "..... the quantitative ratio between the individual sulphides in the ores of different deposits correspond to the ratio of their contents in the stable colloidal solution".

7.2 Sulphide gels.

Experimental investigations of Lebedev (1967) give important information on the development of structures within sulphide gels. He artificially produced zinc sulphide gels in the laboratory from concentrated solutions of sodium sulphide plus zinc sulphate. After about fifteen minutes the initial precipitate consisted of rounded concretions 0.1 - 0.5 mm. in size in a uniform gelatinous mass. The concretions increased to 3 - 4 mm. diameter after addition of more sodium sulphide. This amorphous precipitate transformed to a crystalline mass after heating from 100 - 110° C. After ageing of the amorphous gel for six months, the internal structure consisted of uniform fine globules (0.1 - 0.3) with evenly distributed larger globulites (framboids). The surface layer consisted of coarsely globular aggregates containing large (4 - 5 mm.) sphalerite oolites. X-ray photos of the finely globular gel showed an amorphous nature while the outside crust showed diffuse sphalerite lines. After a year of ageing, well defined crystals had developed in the gel but these had not destroyed the colloform texture initially developed. Lebedev also studied the effect of salts, NaCl and $CaCl_2$ on the ageing of zinc sulphide gels. He found that the presence of NaCl and $CaCl_2$ in the original gel solutions caused a considerable speed up of the ageing processes. After one and one half months of ageing these gels gave X-ray powder photographs showing all the principal lines of sphalerite.

This observation suggests that metal sulphides deposited from ore fluids concentrated in brines are less likely to retain their gel structures

than those deposited from brine-free solutions.

Lebedev extended his experimental work to include a study of two component ZnS + PbS gels. Ageing in two component gel systems in which ZnS predominated led to the separation of three layers:

(a) Top layer of globular ZnS.

(b) Middle layer of globular ZnS and skeletal PbS.

(c) Bottom layer of crystallized PbS particles showing octahedral and cubic-octahedral forms.

The separation into layers was cited by Lebedev as a result of the differing crystallization power of the components and was "..... expressed either as gravitational differentiation of the precipitate or as collective crystallization of particles of one component suspended in another".

It is noteworthy that these experiments show crystallization of minor galena in a ZnS gel produces skeletal growths, whereas crystallization of minor sphalerite in a PbS gel results in globular growth. This is possibly a function of the surface-free energy at the ZnS - PbS gel interface. Lebedev comments that this same relationship between galena and sphalerite is observed in natural metacolloidal[+] sphalerite-galena ores.

7.3 Sulphide foams.

Chukhrov (1965) discusses the work of Durov and Filippova (1959) who consider that the migration of sulphides as colloidal foams may be a significant phenoma. Such foams may develop due to a sharp reduction of the vapour pressure caused by fissuring over boiling solutions containing

[+]Metacolloidal is the term introduced by Wherry (1914) to describe minerals exhibiting a relict colloform structure. No genetic connotation of the term is inferred.

sulphides. Durov and Filippova conducted experiments on colloidal sulphide solutions at 191° C and 12 atmospheres pressure. They established the following sequence which gives the foaming effect in decreasing order;

$$MnS > ZnS > FeS > CoS > NiS > Sb_2S_3 > CuS > Ag_2S > Bi_2S_3$$

Colloidal sulphides may be transported for considerable distances by this mechanism, the foaming capacity increasing with increased concentration.

7.4 Adsorption Experiments.

Preliminary experiments have been carried out by Healy (1968) to study the adsorption of copper, lead and zinc ions onto silica sol particles. The results are illustrated in a diagram showing the variation of surface charge on the silica particles as a function of pH of the dispersion medium, for the three separate cations (fig. 12).

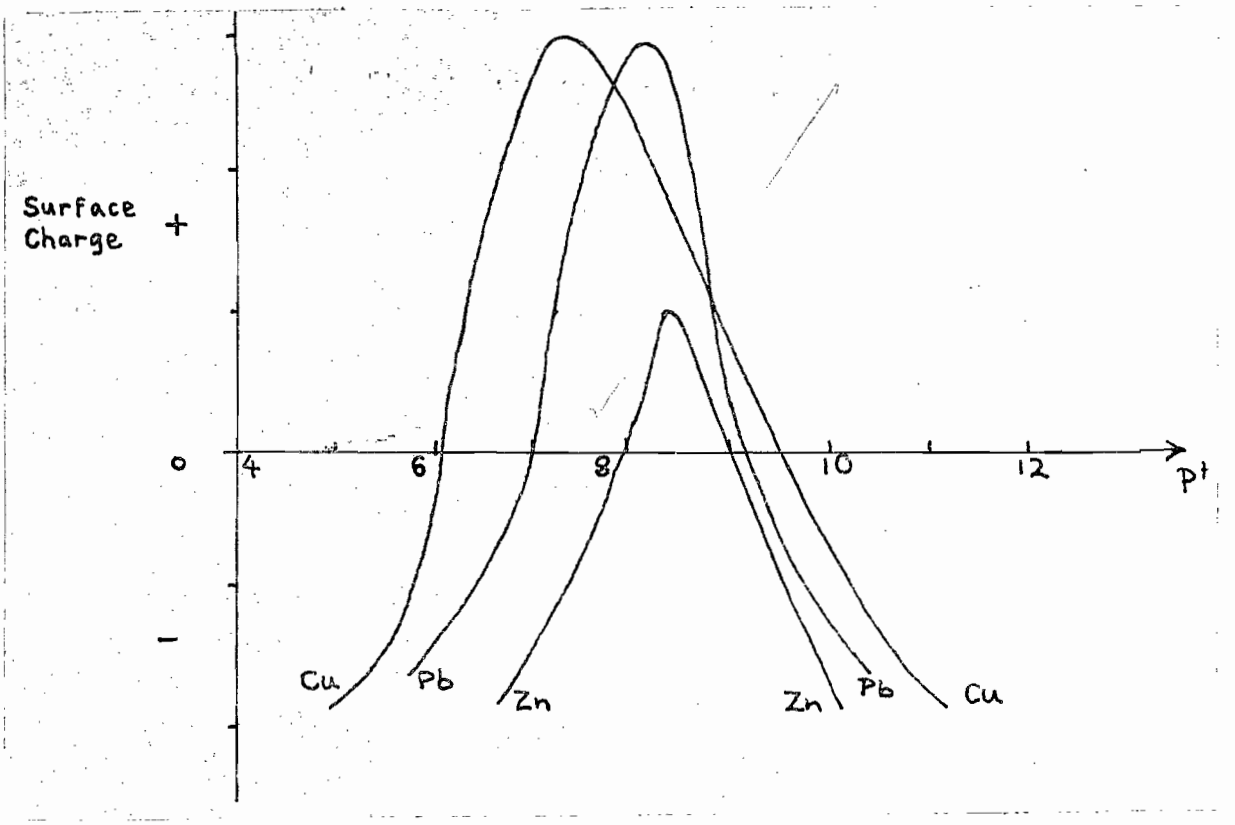


Fig.12. Adsorption curves for Cu^{2+}, Pb^{2+} and Zn^{2+} onto silica sol particles. (Healy, 1968).

Each curve indicates a double reversal of charge, negative to positive to negative, with increasing pH. It is the writer's opinion that the shape of these curves depends on three parameters;

(a) The dissociation constant of the metal hydroxide.

(b) Adsorbability of the metal ion onto the silica surface.

(c) The pH at which Z.P.C. occurs for the metal hydroxide.

Considering the adsorption curve for Cu^{2+}; at pH5, the silica surface is strongly negatively charged with little adsorbed Cu^{2+} ions. With increasing pH, OH^- ions become more abundant in solution and thus in order to maintain constancy of the solubility product (K_{sp}) of $Cu(OH)_2$ *, Cu^{2+} ions must pass out of solution and become adsorbed onto the surface. Consequently the negative surface charge is reduced because of the counter sign of the Cu^{2+} ions. The first reversal of charge occurs when the number of adsorbed Cu^{2+} ions exceeds half the number of $-\overset{|}{\underset{|}{Si}}-O^-$ sites present on the silica surface. As the pH increases, the positive surface charge increases until no more Cu^{2+} ions can be adsorbed. This pH of maximum metal ion adsorbability (M.M.A.) will depend on the dissociation constant of the metal hydroxides in solution. For pH greater than this value the solubility product of $Cu(OH)_2$ can only be kept constant by the adsorption of OH^- ions onto the adsorbed Cu layer surrounding the silica sol particles. This results in a decreasing positive surface charge which reaches zero when the adsorbed OH^- ions neutralize the effect of the adsorbed Cu^{2+} ions. This pH corresponds to the Z.P.C. of $Cu(OH)_2$. At greater pH the surface increases in negative charge due to further adsorption of OH^- ions. This is a very simplified description of

* $K_{sp\ Cu(OH)_2} = \left[Cu^{2+}\right]\left[OH^-\right]^2$

how the adsorption process may occur, and in fact the formation of hydrated copper species may play a more important part. In summary, the first half of the curve represents adsorption of the metal ion, and the second half, adsorption of the hydroxyl ion. It is important to note that for pH values greater than M.M.A., the silica particles have assumed the properties of the metal hydroxide.

The curves in fig. 12. indicate;

(a) for pH $<$ 8.5 (approx.) the order of adsorbability is Cu $>$ Pb $>$ Zn.

(b) for pH $\geq$ 8.5 (approx.) the order of adsorbability is Cu $\simeq$ Pb $>$ Zn.

Some dissociation constants for common metal hydroxides at 250° C are;

$Zn(OH)_2$ K = 9.6×10^{-4}

$Pb(OH)_2$ K = 9.6×10^{-4}

AgOH K = 1.1×10^{-4}

The first two values confer with the results obtained by Healy (196) in the above experiment, that is, the pH at M.M.A. for Pb^{2+} and Zn^{2+} are approximately equal, but greater than that for Cu. It would be expected that Ag^{+} would give an adsorption curve with M.M.A. removed to the right compared with Pb^{2+}. Further experiments of this type, on other metal ions, are necessary to check theoretical predictions such as the above.

8. ORE DEPOSITS OF SUGGESTED COLLOIDAL ORIGIN.

8.1 Shakh-Shagaila tin deposit.

Lebedev (1967) described a cassiterite-quartz-sulphide deposit associated with a granite intrusion located in the north-eastern border zone of the Kaib massif. The ore is restricted to the brecciated central portion of the granite mass where it occurs as veins transecting quartz-topaz-muscovite greisen. The minerals of this deposit are reported by Lebedev to show a great variety of textural types, with almost all varieties of spherical aggregates represented. There is a complete transition from colloform ores through to those exhibiting crystalline-granular and drusy textures. Cassiterite in the veins shows textures ranging from idiomorphic crystalline segregations, through clotty segregations to colloform aggregates (globules, globulites, oolites and reniform textures).

Lebedev (p.141) gives the following as a possible process of mineralization and vein filling. A complex SiO_2 + SnO_2 gel was deposited in veins and cavities in the greisens. Initial ageing of the gel promoted a primary segregation into layers with the formation of monomineralic masses. Subsequent contraction of the gel led to the formation of a central void and also caused exfoliation of the gel mass from the cavity walls. At this stage the siliceous gel had crystallized to a fine grained colloform texture. Interstitial solutions extruded from the gel carried silica in true solution and deposited this as crystalline aggregates on the cavity walls. These solutions became undersaturated in silica resulting in the re-solution of fine colloform grains. Thus, the development of coarse quartz crystals near the cavity walls was accompanied by solution of colloform quartz near the centre.

Colloidal processes may also play a rôle in the genesis of other

cassiterite quartz deposits with ores showing partial metacolloidal textures.

8.2 Mississippi Valley type deposits.

These include lead-zinc deposits generally with fluorite-barite gangue occurring in veins, cavities or as replacements within limestone horizons. Colloform textures, especially in the sphalerite, is a typical feature of these ores. Many theories have been proposed for their genesis but generally the participation by colloids is regarded as unimportant. The following features have been cited by Lasky (1930) and Rust (1935) to support a participation by colloids.

(a) Colloform textures of the common minerals, for example, banded reniform sphalerite, framboidal pyrite and chalcopyrite.

(b) The paragenetic sequence of the copper minerals generally follows the series chalcopyrite, bornite, covellite, chalcocite. This is in exact correspondence with the order of coagulation observed experimentally by Tolman and Clark (1914).

(c) Limestones are ideal coagulators for sulphide sols. (Tolman and Clark, 1914; Clark and Menaul, 1916).

Although a recent publication by Roedder (1968) denies the genetic connotation of the term "colloform", it cannot be disputed that colloform textures have been produced from aged gels in the laboratory. Thus, a possible gel stage for the Mississippi Valley type ores must be recognised. It is invalid though, to assume a sol stage in the transport of the metals; as have Lasky (1930) and Rust (1935). These authors place considerable emphasis on the order of precipitation of the copper minerals. This is an order of increasing copper and decreasing iron content, which Rust (1935) considers to be the controlling factor on the change of the sulphide sol

particles. The solubilities of the copper sulphides show no correlation with this sequence, although the same paragenesis is observed in other deposits which have no inferred colloidal associations.

Rust (1935) considers coagulation of the sulphide sols in the Cornwall Mine, south-western Missouri, was brought about by three factors;

(a) Drop in temperature and pressure as the colloidal solutions rose to the surface.

(b) Removal of the peptizing agent, H_2S, due to (i) diffusion resulting from decreased pressure, (ii) reaction with limestone country rock, and (iii) dilution by ground water.

(c) Coagulating agents in the country rock, such as, limestones, dolomites and aluminous material.

He combines the effects of (b)(ii) and (c) in the reaction;

$$2CaCO_3 + 2H_2S \rightleftharpoons Ca(HS)_2 + Ca(HCO_3)_2$$

(see section 7.1 for the mechanism of this reaction).

An interesting study which may give results to support the colloidal sol theory of transportation could be carried out on the gangue minerals, barite and fluorite, to determine their relative coagulation if transported as sols. The zoning, fluorite, fluorite-barite, barite outwards from the centre of these lead-zinc fields may be explained by a decreasing pH of the sol carrying ore fluids. The pH at Z.P.C. for CaF_2 and $BaSO_4$ sols will depend largely on the dissociation constants of their hydroxides, $Ca(OH)_2$ and $Ba(OH)_2$. (values for these dissociation constants are not available in the chemical literature)

If $\text{Z.P.C.}_{CaF_2} < \text{Z.P.C.}_{BaSO_4}$, then the following coagulation sequence is observed with increasing pH.

(i) CaF_2 coagulates at the pH of Z.P.C.$_{CaF_2}$

(ii) CaF_2 and $BaSO_4$ mutually coagulate due to opposite particle charges at Z.P.C.$_{CaF_2} \ll pH \ll$ Z.P.C.$_{BaSO_4}$

(iii) $BaSO_4$ coagulates at the pH of Z.P.C.$_{BaSO_4}$

Edwards (1947) suggests that colloform ores develop in limestones because of the availability of open spaces which permit rapid precipitation of the sulphides from true solutions. Limestones are readily susceptible to solution by the ore fluids whereas mudstones, sandstones, etc., do not provide the cavities necessary for rapid precipitation.

Many workers, such as Beales and Jackson (1966), Noble (1963), consider colloids play an indirect part in the genesis of the Mississippi Valley type ores. Shale sequences associated with the host limestones are known to contain sufficient quantities of syngenetic lead and zinc to account for any of the ore bodies, provided there exists a method of metal concentration A high proportion of the lead and zinc in these sediments can be accounted for by the adsorption of metal ions onto colloidal clay particles during deposition. Under a depth of burial of 500 feet the saturated clay sediment has its water content reduced from about 80% to 35% (Noble, 1963). With continued compaction the pore water and adsorbed ions are squeezed out from between aggregating clay particles. Beales and Jackson (1966) consider that these ions may pass into solution as the complex chlorides and are carried upwards and laterally by the expelled connate waters. The ions are then precipitated as sulphides due to the interaction with H_2S entrapped in the pore spaces of the limestones. They maintain that limestones contain entrapped gases with much higher percentages of H_2S than do sandstones, shales, etc. In the lead and zinc districts

of the Upper Mississippi, Noble (1963) believes the deposits lie along major channel ways for the discharged formation water.

8.3 Miscellaneous deposits.

Anderson (1963) describes silver mineralization in the Mineral District, Washington County, Idaho. He reports the silver bearing ore as very fine grained, being composed of galena, chalcopyrite, tetrahedrite, pyrite, marcasite, sphalerite and wurtzite, plus minor sulpho salts. It occurs filling fractures and as replacement within broad zones of complexly fractured and altered volcanic rocks. The majority of mineral types display metacolloidal textures. Pyrite, for example, occurs as globules, framboids and reniform masses, but may also form independent crystals or granular aggregates. Sphalerite also shows a metacolloidal nature and commonly occurs as concentric bands molded on the surface of reniform and globular pyrite. Zinc sulphide may replace radiating crystals of pyrite and marcasite within reniform masses of these minerals.

Anderson accepts the metacolloidal textures of the ores as "indisputable support" for colloidal deposition of the iron and zinc sulphides. He concludes that since the minerals younger than sphalerite in the paragenetic sequence do not show metacolloidal textures, then all the constituents were probably carried in ionic solution. The iron and zinc sulphides were the only ores to pass through the gel stage during precipitation and crystallization. This is not the only deduction possible, but is the simplest, considering the facts available. Diffusion of Zn^{2+} ions through the ageing iron sulphide gels may have produced the replacements observed.

The Lokun'zh lead-zinc deposit has been studied in detail by Lebedev (1967). This is a lead-zinc cavity filling deposit generally

restricted to Upper Cretaceous limestones in the north-western foothills of the Darvezz Range. Lebedev describes sphalerite-galena lenses which commonly have festooned sphalerite layers at their contacts, with galena and sphalerite pisolites constituting the main mass. In all cases the pisolites increase in size from the footwall to the hanging wall of the lenses. The galena pisolites carry a minor percentage of sphalerite in concentric bands and vice versa. Fluid inclusions in galena occurring in breccia zones contain major concentrations of Mg^{2+}, Na^{2+}, H_2S and Cl^-.

Lebedev proposes that the ore fluid probably separated from the source melt as an aerosol*. This later graded into a hydrosol in which zinc sulphide and lead sulphide particles were dispersed in a complex ionic solution containing sodium and magnesium sulphides. Coagulation of the zinc and lead sulphides was caused by the introduction of Ca^{2+} ions into the solution as the ore fluid passed into the limestone horizon.

The Kerch Sedimentary iron ores are cited by Andreyeva and Sedletskiy (1967) as a deposit formed by mutual coagulation of negatively charged colloidal clay particles and positively charged iron hydroxide particles. Electron-micrographs of the ore depict globules and globulites of iron hydroxide, attached to, and permeating flaky clay crystals of hydromica and kaolinite. In electrophoretic experiments the fine grained ore broke up into two factions; the clay particles collected at the anode and the iron at the cathode. Andreyeva and Sedletskiy consider that the colloidal clay and iron hydroxide must have been separately transported to their coagulation point, (a shallow marine basin) where they settled to form iron ores rich in clay.

Elliston (1966) proposes a colloidal genesis for the Peko Orebody,

* An aerosol is the colloid system of solid particles dispersed in a gas phase.

Tennant Creek, based on the remobilization of clay rich sediments. The ore occurs in a pipe-like structure located in the southern limits of a west plunging syncline. The pipe transects a sequence of subgreywackes and shales which conformably overlie porphyroidal rocks. The ore bodies consist of massive magnetite, haematite and sulphides in a quartz-chlorite-sericite gangue. Wright (1969) describes mammilliary structures in magnetite, quartz, jasper and chalcopyrite-sphalerite. Botryoidal textures are less numerous but occur in jasper, magnetite, dolomite and haematite. Leisegang type banding of iron oxide in dolomite has been reported, although calcium carbonate gels have never been reproduced in laboratory experiments (Kraushoff, 1967). Accicular crystal clusters, "filamentous" crystals and radial crystal aggregates have been cited by Wright (1969) as evidence of crystal growth within a gel medium.

Elliston (1966) agrees with the views of Noble (1963) in that connate water expelled from the sediments is the source of the mineralizing fluid. But he considers that the metal ions adsorbed onto clay particles in the original sediment cannot have been desorbed without a process of sediment reslurrying with later reconstitution. He maintains that the sediments must have been subjected to a physical shock or shear (earthquakes, tilting) which enabled thixotropic reliquification producing a very mobile unit calable of intruding other sediments. Colloidal particle aggregates containing adsorbed metal ions developed within the remobilized sediment. Compaction and dehydration resulted in desorption of the metal ions, which then aggregated to form colloidal hydrosols which were forced out of the lithifying sediment along zones of weakness. Colloidal matter recrystallized in the sediments to form a porphyroidal rock with an "igneous type" texture.

The colloidal hydrosols were peptized by silica plus other sol dispersions, and precipitated in the Peko ore pipe by concretion.

A fundamental problem with the theory proposed by Elliston is that the porphyroidal source rocks are not indisputably recognised as retextured sediments. In fact, recent work by Duncan (Pers. comm.) indicates that some (e.g., Great Western Reopelite) are definitely of volcanic origin.

9. COLLOIDAL SOLS VERSUS TRUE SOLUTIONS AS THE ORE FLUID.

Using information derived from thermal springs, fluid inclusions, phase relations and thermo-chemical parameters, Helgeson (1964) concludes that ore forming fluids consist of alkali chloride rich electrolytic solutions containing predominantly Na^+ and Cl^-, lesser amounts of K^+ and Ca^{2+}, small amounts of $SO_4^=$, $CO_3^=$, HCO_3^-, Li^+, Cs^+ and minor amounts of constituents such as sulphide and the ore forming metals. Barnes (1967) considers H_2S and NH_4^+ are also important constituents.

The effectiveness of the colloidal sol in carrying the metal must depend on its stability in the ionic environment proposed above. Barnes (1967, p.337) sums up the opinion of many ore geologists in his statement, "Colloidal transport.....may be dismissed because colloids are unstable in electrolyte solutions such as the brines of fluid inclusions and ore solutions, and are most probably thermally unstable as well". At present, the theory of stability of complex colloidal sol systems is in such a preliminary state of development, that Barnes' statement is quite unacceptable. No experiments have been carried out on systems containing more than two sol species in the ionic environment described by Helgeson (1964). The effect of temperature, pH, hydrogen sulphide and the concentration of other ions, are of major importance in the stability of colloidal sols, and have not been stutied in sufficient detail to allow generalised statements such as that of Barnes.

Most simple colloidal sols require a low concentration of electrolyte to maintain a particle charge and become dispersed. But a high concentration of electrolyte may cause coagulation. The exact concentration to cause coagulation varies markedly for different electrolytes and different

sols. In fact, Krauskopf (1967) points out that some sols (e.g., Ag in a solution of NaCl), are stable in both dilute and concentrated electrolytes but not in the intermediate range.

From experimental work Barnes (1967) concludes that in acidic solutions (pH <7) saturated in H_2S, the solubilities of the simple sulphides (ZnS, CuS, PbS and Ag_2S) are less than 5 mg l^{-1}, which is too low to account for even the smallest orebodies. In the environment of stable bisulphide (HS^-) ions, (approx. $7 < pH < 13$), these metals form significantly soluble bisulphide complexes, which are proposed by Barnes to be an ionic species by which these metals may be transported in the ore solution. Helgeson (1964) claims the pH of ore solutions at low temperatures may range from three to about nine. Thus for more than half the pH range of geological environments, bisulphide complexing cannot account for significant metal ion transportation. Also, to form the stable bisulphide complexes Barnes requires very high concentrations of H_2S and HS^- ions, for example; CuS has a solubility of 1300 mg l^{-1} at 204° C, 24 atmospheres and 4.1 m NaHS. Helgeson points out that fluid inclusions and thermal spring data definitely do not indicate such high concentrations of total sulphur. He claims that the metals are transported as ionic chloride complexes. This meets with a problem of origin and transportation for the sulphur.

The preceding discussion indicates that considerably more experimental work must be carried out on complex ionic and colloidal systems under geological environments before any conclusive assessment of the topic can be attempted.

CONCLUSIONS.

In concluding this review the writer feels that the following points are of major significance.

(a) The lack of colloidaltextures and the existence of the idiomorphic crystalline expression in a suite of minerals does not conclusively indicate a non colloidal origin. Crystallization from a dispersed sol or coagulated gel has been proved beyond doubt in the laboratory.

(b) There is no interdependence between transport of metals as the sol and their deposition as the gel. That is, gels may result from coagulation of a sol or precipitation from concentrated true solutions, while a sol may coagulate as the gel or precipitate as a crystalline aggregate.

(c) Colloform textures commonly show development in near-surface ore deposits, but they have also been observed at considerable depths. Chukhrov (1965) concludes that the following factors may be effective in producing gel precipitates from a hydrothermal ore fluid, (i) a sharp drop of external pressure, (ii) rapid cooling of the solutions, and (iii) their encounter and mixing with vadose waters.

(d) Fluid inclusions present in mineral aggregates which have developed due to the ageing of a colloidal gel precipitate, may have little relationship with the depositing fluids. This is apparent when it is realized that the pore fluids in a coagulated gel contain much higher concentrations of electrolytes than the surrounding fluids. The ionic species which make up the concentrated interstitial electrolytes, constitute those ions which were adsorbed onto the original sol particles and become entrapped in the pores during coagulation. Upon ageing and crystallization, any inclusions which develop, will be filled with the interstitial fluids, rather than the external

fluids from which the gel originally precipitated.

(e) It is the writer's opinion that future research work in this field must include;

(i) Collection of all present experimental data on the stability of the hydrosols important in geological environments, (sulphides, hydroxides, silicates, oxides, etc.)

(ii) An experimental study of the factors effecting the Z.P.C. condition of metallic sulphide hydrosols (both simple and compound sulphides.)

(iii) Determination of the order of peptization of the simple and compound sulphide hydrosols by hydrogen sulphide. The effect of pH on this peptization sequence.

(iv) Experimentation of determine the flocculation values of NaCl, KCl, $CaCl_2$ and $CaCO_3$ on sulphide hydrosols, (I) peptized by hydrogen sulphide and (II) protected by silica.

(v) Studies on the stability of peptized hydrosols at increasing temperature and pressure and within the chemical environment proposed by Helgeson (1964) (see section 9.)

(vi) Experimental determination of the pH at Z.P.C. for the hydrosols of common gangue minerals such as calcite, fluorite and barite.

(vii) A study of the fluid inclusions of colloform and crystalline ore minerals to determine whether compositional differences exist between the two varieties (as is predicted in (d) above.)

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